Supporting Information for:

Heck Coupling of Olefins to Mixed Methyl/Thienyl Monolayers on Si(111) Surfaces

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A. XP spectra

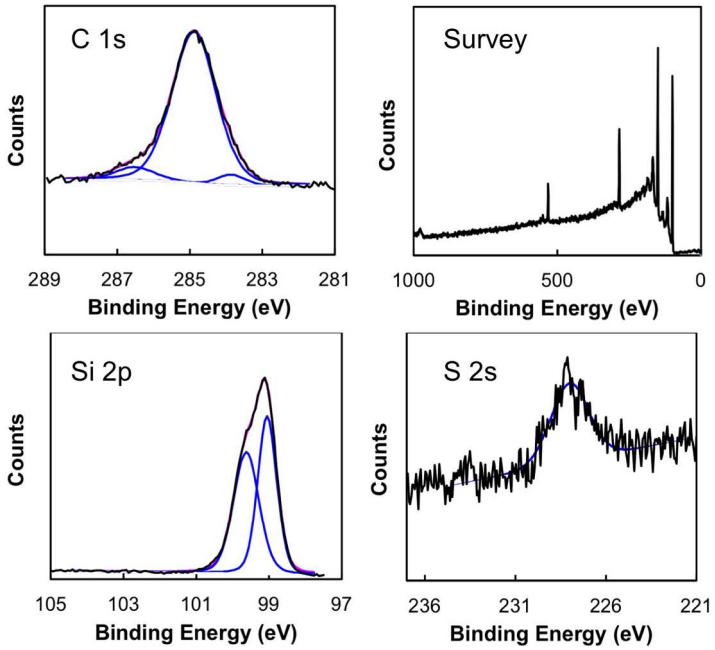


Figure SA1. C 1s (100 scans), Si 2p (40 scans), S 2s (200 scans), and survey (4 scans) XP spectra of a mixed CH_3/SC_4H_3-Si(111) with $\theta_{SC_4H_3} \approx 0.20$.

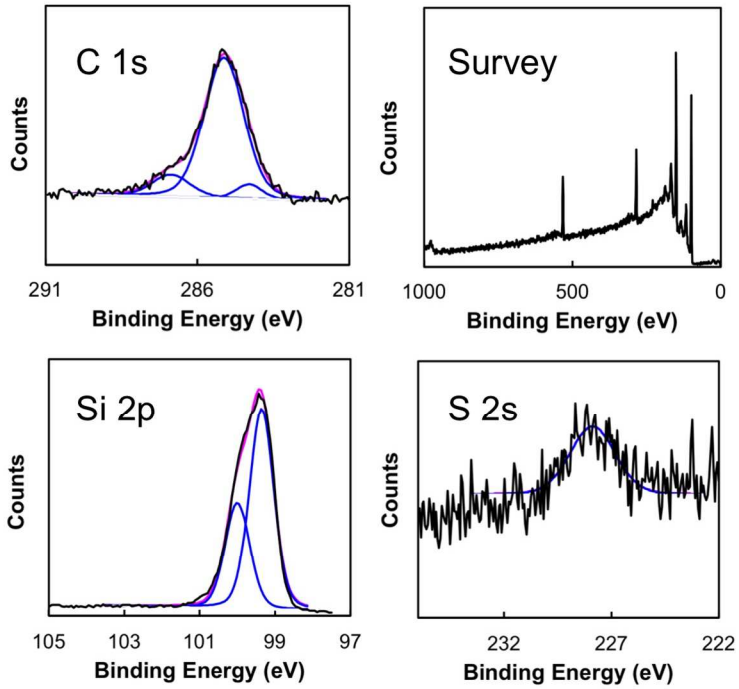


Figure SA2. C 1s (15 scans), Si 2p (20 scans), S 2s (30 scans), and survey (2 scans) XP spectra of a mixed CH_3/SC_4H_3-Si(111) with $\theta_{SC_4H_3} \approx 0.35$.

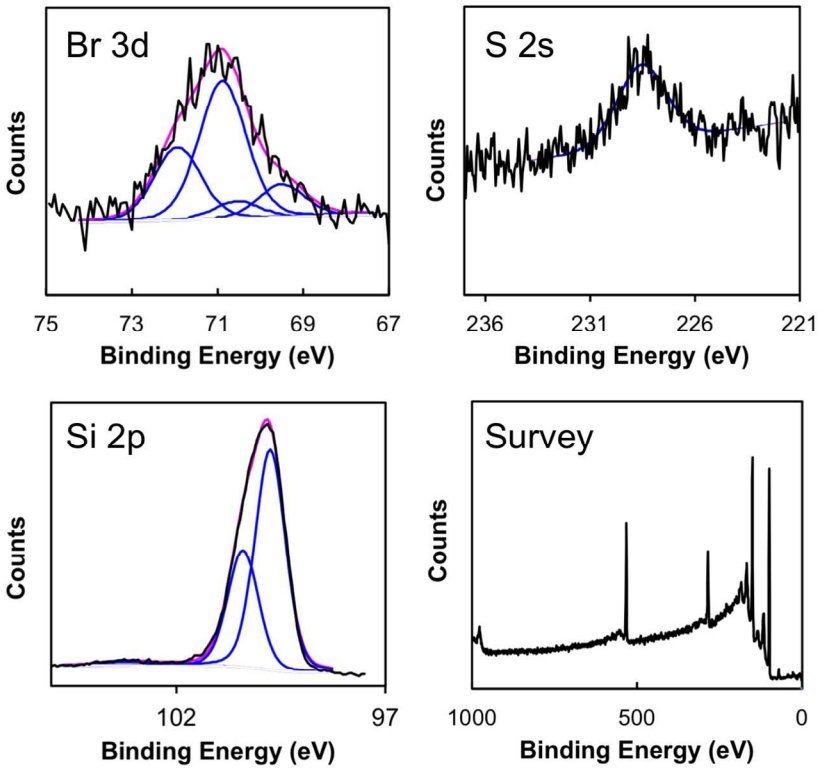


Figure SA3. Br 3d (50 scans), Si 2p (30 scans), S 2s (60 scans), and survey (4 scans) XP spectra of a mixed CH_3/SC_4H_2Br-Si(111) with $\theta_{SC_4H_3} \approx 0.25$, $\theta_{Br\text{-}SC_4H_2} = 0.16$, and $\theta_{Br\text{-}Si} = 0.05$.

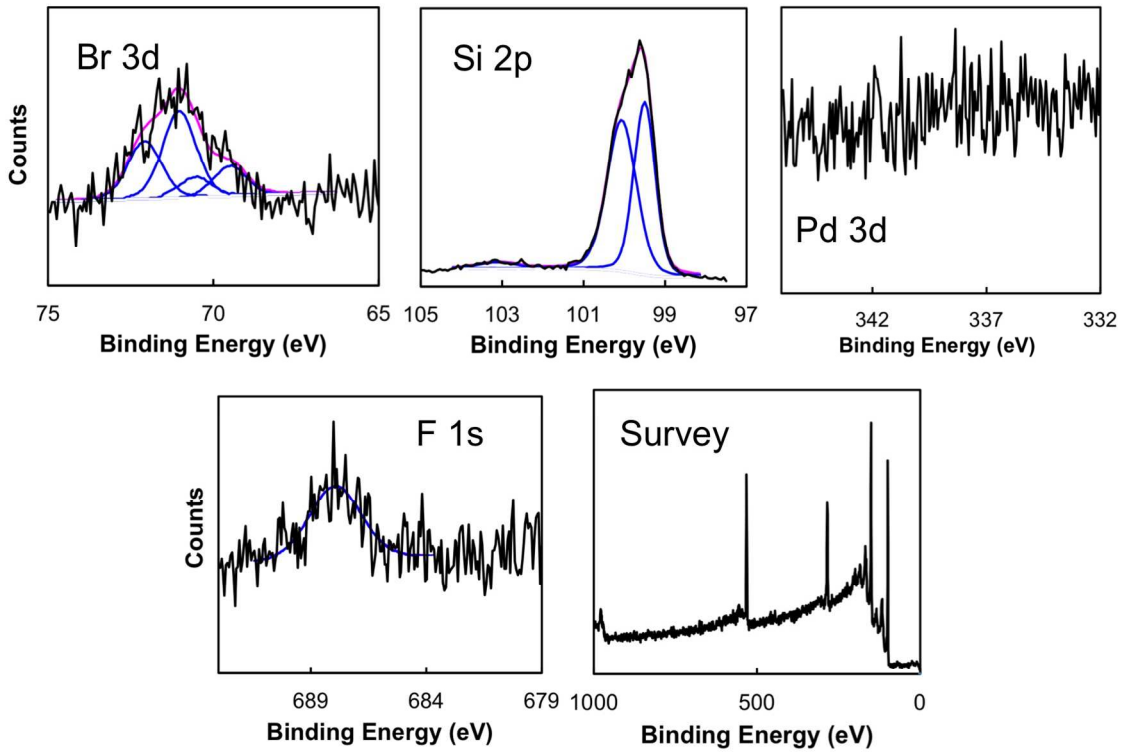


Figure SA4. Br 3d (100 scans), F 1s (120 scans), Pd 3d (120 scans), Si 2p (33 scans), S 2s (30 scans), and survey (2 scans) XP spectra of a mixed CH_3/FSty-SC_4H_2-Si(111) with $\theta_{SC_4H_3} \approx 0.20$ and $\theta_{FSty} = 0.11$.

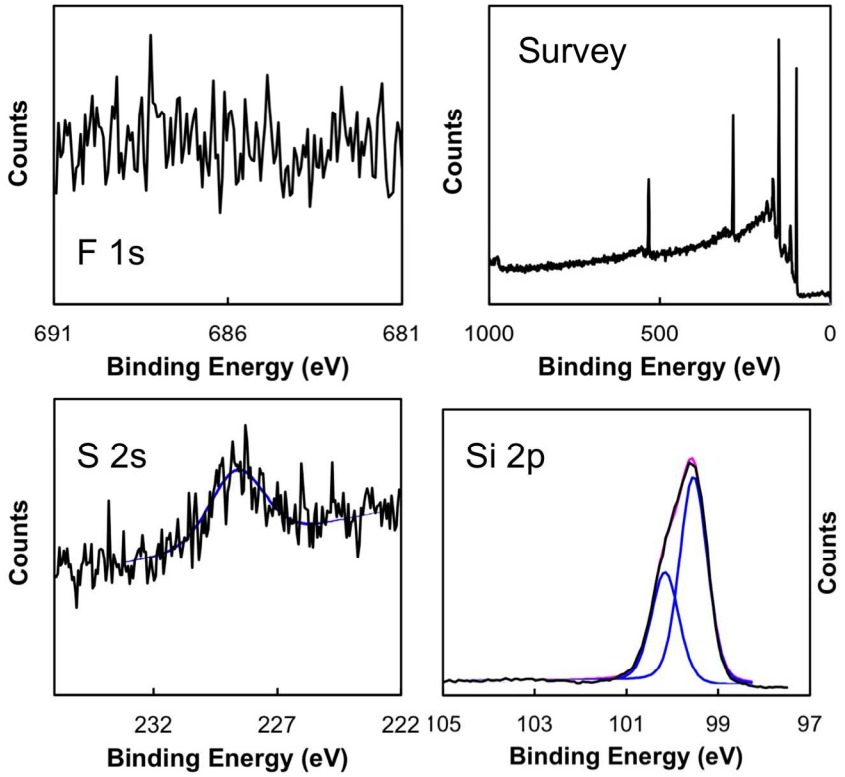


Figure SA5. F 1s (150 scans), S 2s (200 scans), Si 2p (70 scans), and survey (4 scans) XP spectra of CH_3/SC_4H_3-Si(111) after exposure to $Pd(PPh_3)_4$ (toluene, RT), then 4-fluorostyrene (DMF, 100 °C), but with no exposure to NBS. No F was detected using XPS.

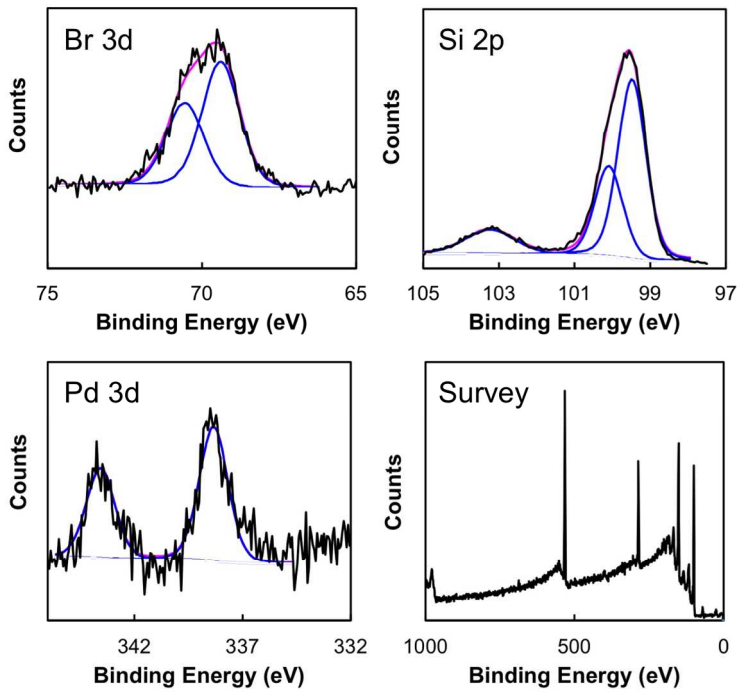
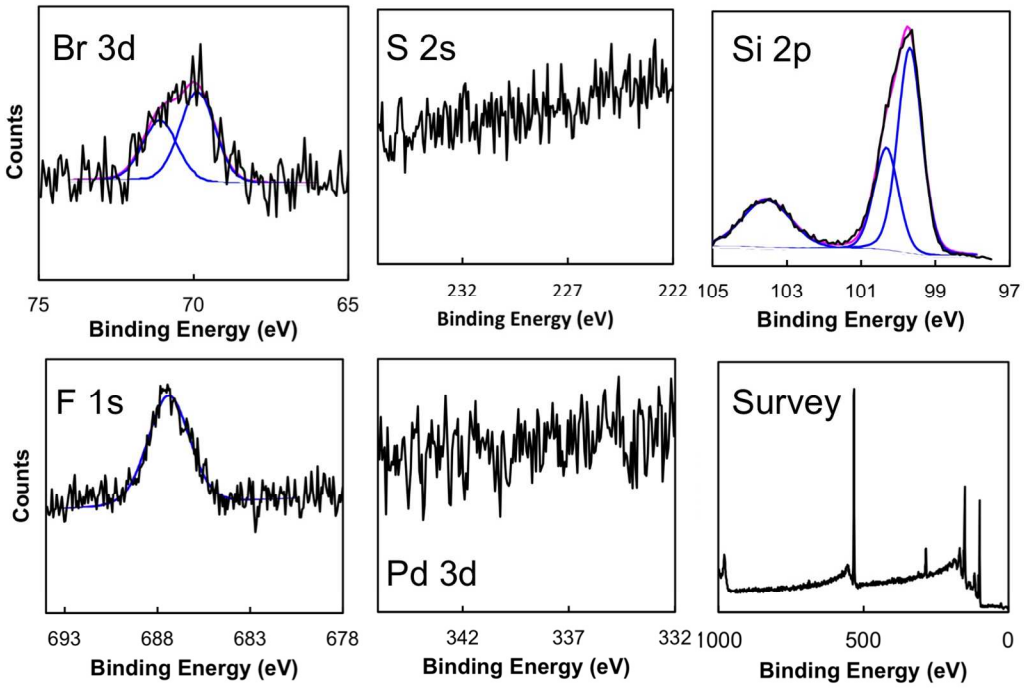


Figure SA6. Br 3d (250 scans), Pd 3d (250 scans), Si 2p (70 scans), and survey (40 scans) XP spectra of a Br-Si(111) surface after exposure to $Pd(PPh_3)_4$ (toluene, RT). θ_{Pd} = 0.06.



Figures SA7. S 2s (150 scans), Br 3d (200 scans), Pd 3d (200 scans), F 1s (100 scans), Si 2p (20 scans), and survey (4 scans) XP spectra of Pd activated Br-Si(111) after reaction with 4-fluorostyrene (DMF, 100 °C). Pd catalyzed hydrosilylation takes place under these conditions.

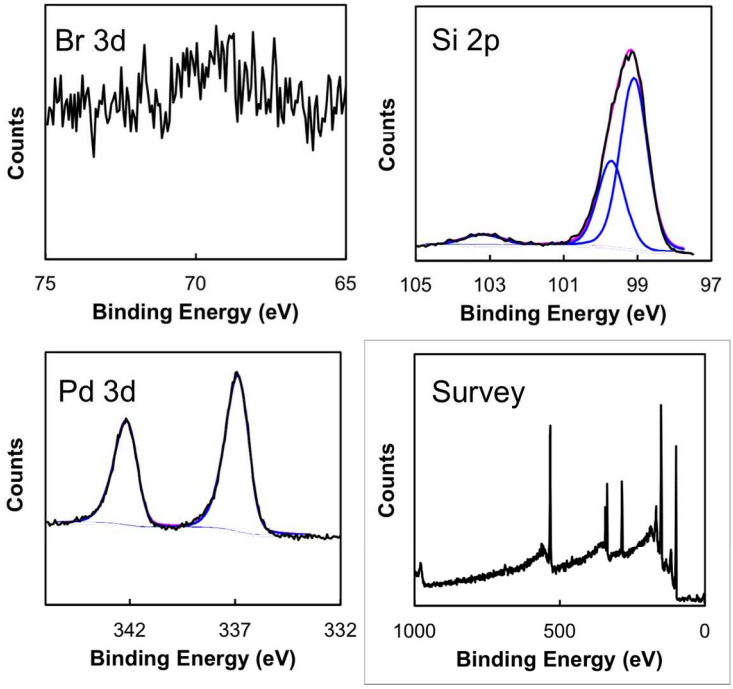


Figure SA8. Br 3d (250 scans), Pd (250 scans), Si (70 scans), and survey (4 scans) spectra of H-Si(111) after exposure to $Pd(PPh_3)_4$ (toluene, RT).

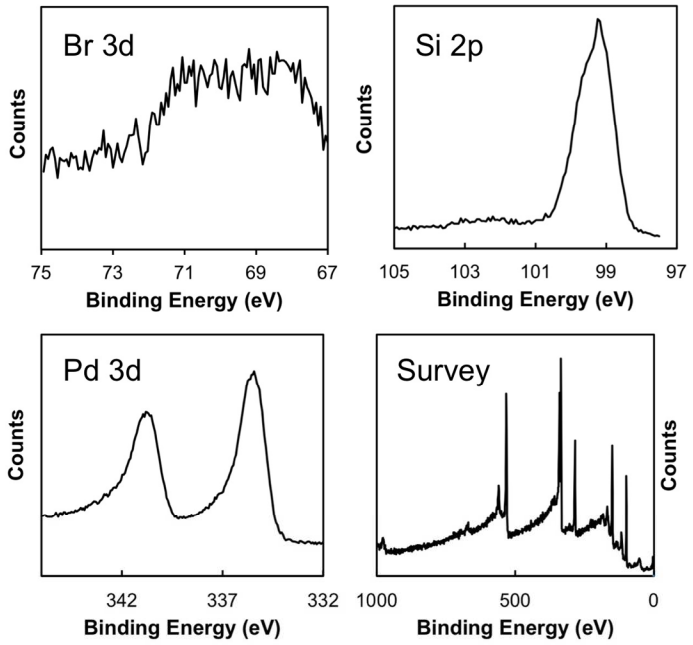
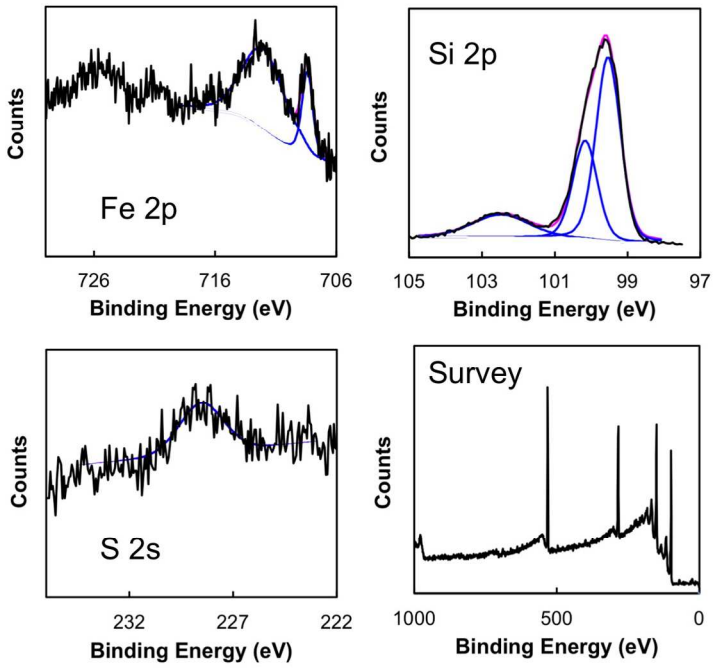


Figure SA9. Br 3d (150 scans), Si 2p (40 scans), Pd 3d (100 scans), and survey (4 scans) spectra of CH_3/SC_4H_2Br-Si(111) surfaces after exposure to $Pd(dba)_2$ (toluene, RT).



Figures SA10. Fe (200 scans) XP spectrum of the CH_3/Fc-SC_4H_2-Si(111) surface after cyclic voltammetry experiments. $\theta_{Fe} = 0.082$, and $\theta_{SC_4H_3 + SC_4H_2\text{-}Fc} = 0.24$.

B. Cyclic Voltammetry

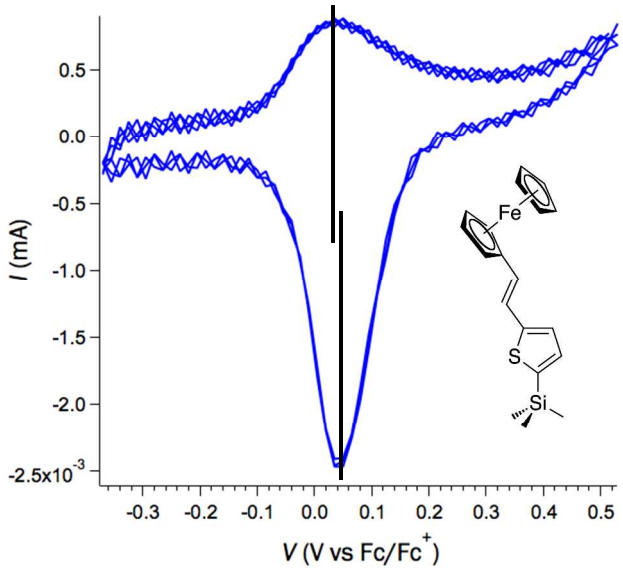


Figure SB1. Cyclic voltammogram of vinyl ferrocene modified n-Si, $\theta_{Fc} = 0.12$. 1.0 M $LiClO_4$ in acetonitrile, 2500 mV s^{-1}. The asymmetry is due to the electron transfer dynamics at non-degenerately doped semiconductor electrodes. The small splitting, 0.01 V, between the potentials where the cathodic and anodic currents exhibited peaks suggests facile electron transfer through the conjugated linker.

C. Substrate overlayer model

The substrate overlayer model can be used here, as described in the text:

$$d_{ov} = \ln\left[\left(\frac{I_{ov}}{I_{Si}}\right)\left(\frac{SF_{Si}}{SF_{ov}}\right)\left(\frac{\rho_{Si}}{\rho_{ov}}\right)+1\right]\lambda\sin(\theta)$$

d_{ov} is the thickness of the overlayer, I_{ov} and I_{si} are the signal intensity of the C_{si} and Si_{bulk} 2p(3/2) XPS signals respectively. SF_{ov} and SF_{Si} are the modified sensitivity factors for the Si 2p(3/2) and C 1s signals. ρ_{ov} (0.14 mol cm^{-3} based on d_{CH3}) and ρ_{Si} (0.083 mol cm^{-3} based on Si crystal structure) are the atomic density of C in the overlayer and in the Si crystal. λ is the mean free path of electrons, determined empirically as 3.5 nm for Si 2p electrons,{haber; laibinis 1991; tufts 1992} and θ is the angle from the horizontal to the detector (35°).

$$SF_x = SF_{scof}\left[\frac{1486-BE}{1486-284}\right]^{S_{exp}}$$

Modified sensitivity factors are calculated based on the binding energy of the electron (BE), and the configuration dependent sensitivity exponent (S_{exp}). In this case, S_{exp} = 0.6 and SF_{Si} = 0.9 for the 2p electrons.

d_{ov} = 0.097 for the CH_3-Si(111) surface. d_o for a methyl group is 0.234 nm, and thus gives 0.41 ML CH_3 groups. 1 monolayer of CH_3 groups having a density of 1.89×10^{15} (based on d_{CH3} = 2.3 Å), gives Γ_{CH3} 8.0×10^{14} cm^{-2} or $\theta_{CH3\text{-}Si}$ = 0.99 ± 0.06 (based on $\Gamma_{Si(111)} = 7.83\times 10^{14}$ cm^{-2}).

Similarly, the fractional overlayer equation

$$\Phi_{ov} = \left[\frac{\lambda\sin\theta}{a_{ov}}\right]\left(\frac{SF_{Si}}{SF_{ov}}\right)\left(\frac{\rho_{Si}}{\rho_{ov}}\right)\left(\frac{I_{ov}}{I_{Si}}\right)$$

gives a similar value of Φ_{ov} = 0.43 or $\theta_{CH3\text{-}Si}$ = 1.04 ± 0.06.

D. Molecular Modelling of Surface Species

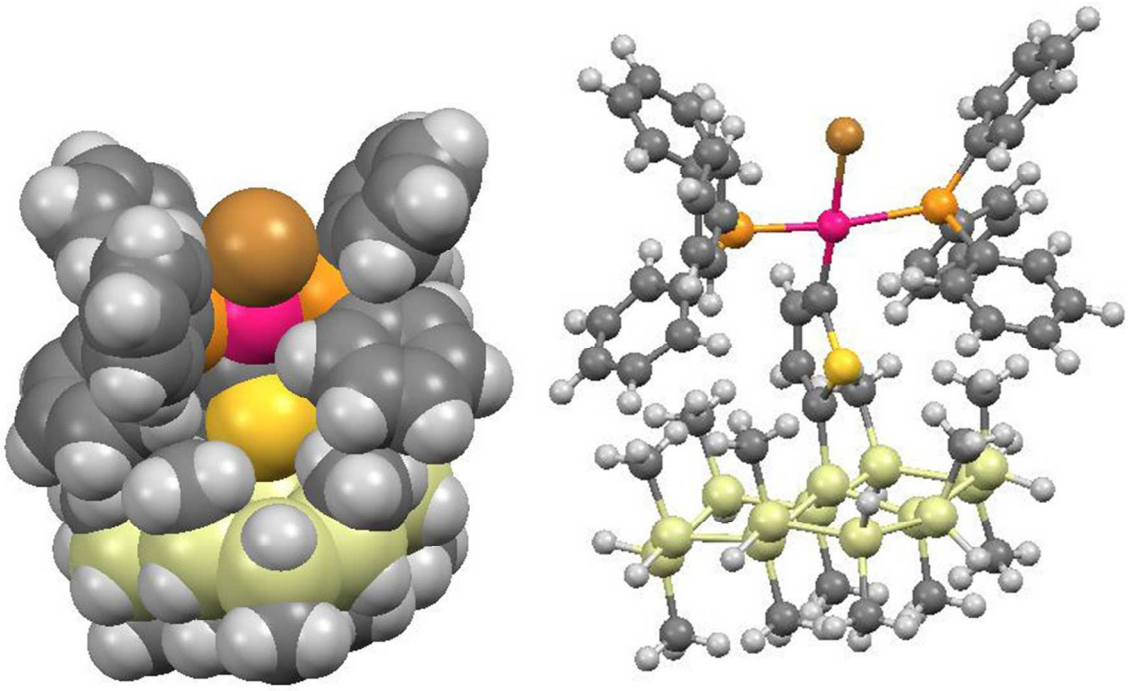


Figure SD1. Geometry optimized molecular model of the proposed Pd-activated species, namely CH_3/Br-Pd(PPh_3)$_2$-SC_4H_2-Si(111), on a small portion of hexagonal Si(111) surface: (left) space-filling model of the species, (middle) ball-and-stick model of the same species, (right) ball-and-stick model of the species with H's omitted for clarity. The overall 'planar' rigidity of the Si(111) framework was in this case was enforced by substituting methyl groups in the basal plane. The Pd-ligated surface was modeled using the 3-21G basis set and the functional PW91.[1] The geometries were optimized to a low root mean square gradient (GRMS < 0.001) in Firefly,[2] and the resulting models were visualized in Mercury.[3]

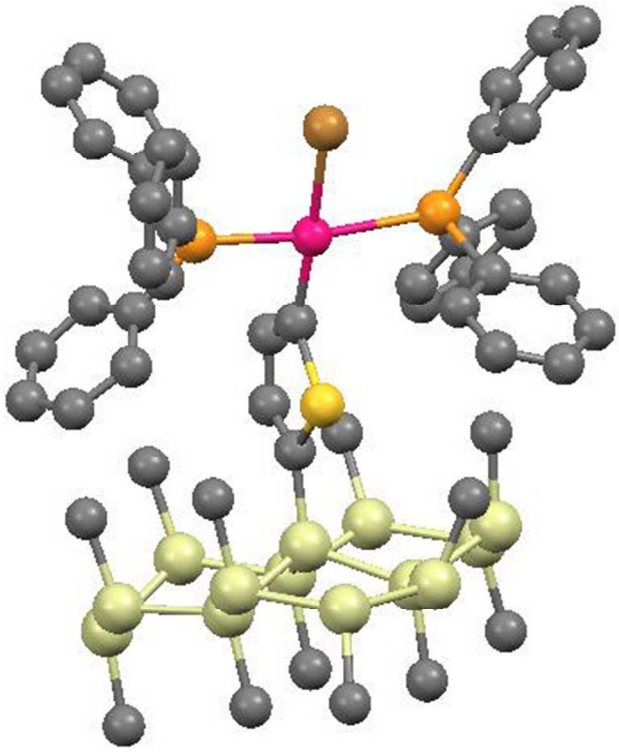


Figure SD2. Geometry optimized molecular model of the proposed Pd-activated species, namely CH_3/Br-Pd(PPh_3)$_2$-SC_4H_2-Si(111), on a small portion of hexagonal Si(111) surface: (above) ball-and-stick model of the species with H's omitted for clarity. The overall 'planar' rigidity of the Si(111) framework was in this case was enforced by substituting methyl groups in the basal plane.The Pd-ligated surface was modeled using the 3-21G basis set and the functional PW91.[1] The geometries were optimized to a low root mean square gradient (GRMS < 0.001) in Firefly,[2] and the resulting models were visualized in Mercury.[3]

References

(1) (*a*) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M.; R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B: Condens. Matter* **1993**, *48*, 4978. (*b*) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B: Condens. Matter* **1992**, *46*, 6671–6687.

(2) Granovsky, A. A. *Firefly, v.7.1.G*; http://classic.chem.msu.su/gran/firefly/index.html

(3) http://www.ccdc.cam.ac.uk/free_services/mercury/downloads/